REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Papers	

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Leilani Richardson
Unclassified	Unclassified	Unclassified	A		19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

62 [illegible]

2303 m2 cp

MEMORANDUM FOR PRS (~~Contractor~~/In-House Publication)

FROM: PROI (TI) (STINFO) 24 June 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0159
S. Tam and M.E. Fajardo, "Quantitative Matrix Isolation Spectroscopy in Heavily Doped Millimeters Thick Parahydrogen Solids"

Gordon Research Conference (International) **(Statement A)**

GORDON CONFERENCE, PHYSICS AND CHEMISTRY OF MATRIX ISOLATED SPECIES
PLYMOUTH, NH, 11-15 JULY 1999

Quantitative Matrix Isolation Spectroscopy in Heavily Doped Millimeters Thick Parahydrogen Solids

Simon Tam and Mario E. Fajardo
U.S. Air Force Research Laboratory, Propulsion Directorate
(AFRL/PRSP, 10 E. Saturn Blvd. Edwards AFB CA 93524-7680
simon_tam@ple.af.mil
mario_fajardo@ple.af.mil

ULD Slide

TASK OBJECTIVE

Develop a technique for quantifying dopant species identities and concentrations in optically dense samples using the dopant-induced infrared (IR) absorptions.

BACKGROUND

Have demonstrated we can produce gram scale samples of solid pH_2 doped with HEDM species with concentrations of 0.01 to 0.1%.

Dopants were produced using laser ablation which is not a suitable method for producing high concentrations.

Three teams in the Cryosolids Working Group tasked with: 1) developing new dopant sources; 2) developing a diagnostic for characterizing the new sources; and **3) developing diagnostic tools for detecting the products of these new sources in pH_2.**

APPROACH

Direct absorption measurements of thick, heavily concentrated samples of HEDM doped pH_2 solids will not work as a diagnostic for these new sources.

Alternative is to use the dopant-induced IR absorptions as a diagnostic.

OLD SLIDE

High Energy Density Matter (HEDM) Cryosolid Propellants

HEDM Cryosolid Program Objectives

Trap 5% molar concentration of energetic additives in solid hydrogen.
Demonstrate size-scaleable sample production method.

Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

LOX/LH_2: I_{sp} = 390 s
5% B/H_2 + LOX: I_{sp} = 500 s (+30%)*

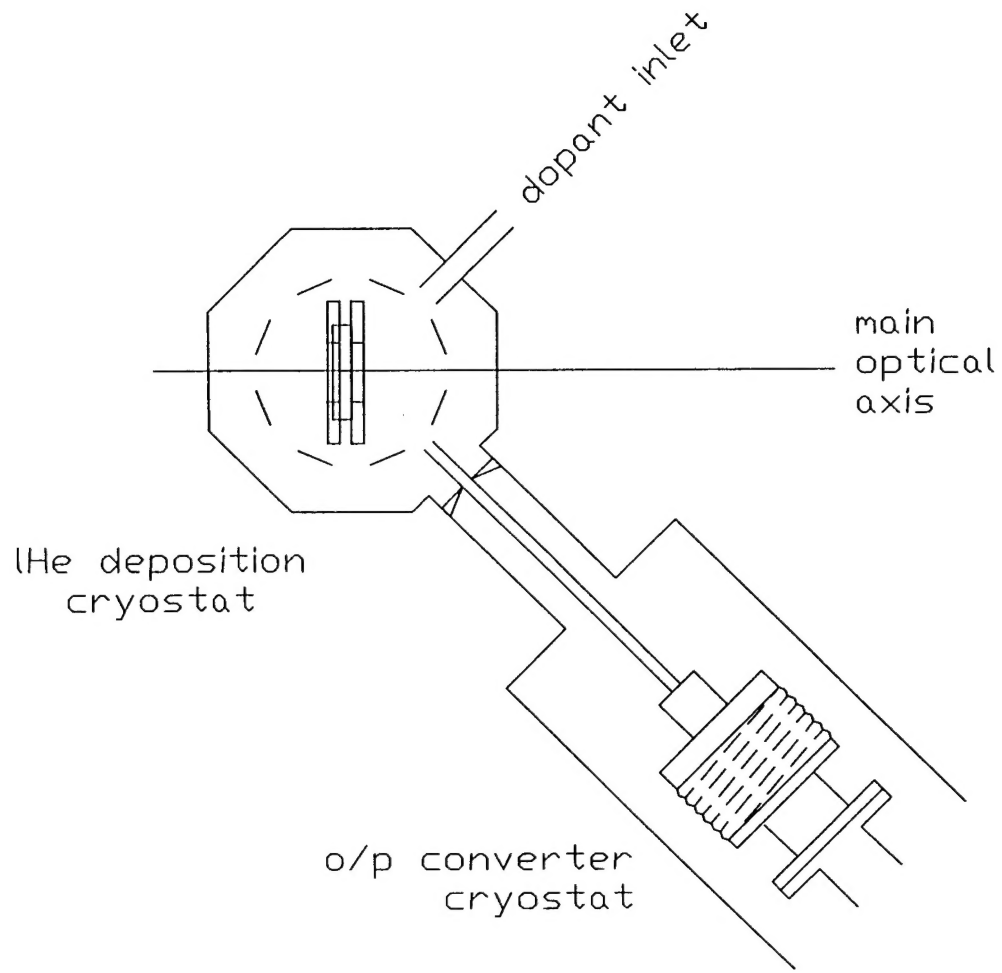
*calculated for $P_{chamber}$ = 1000 psia, $P_{exhaust}$ = 14.7 psia

Greater Propellant Density

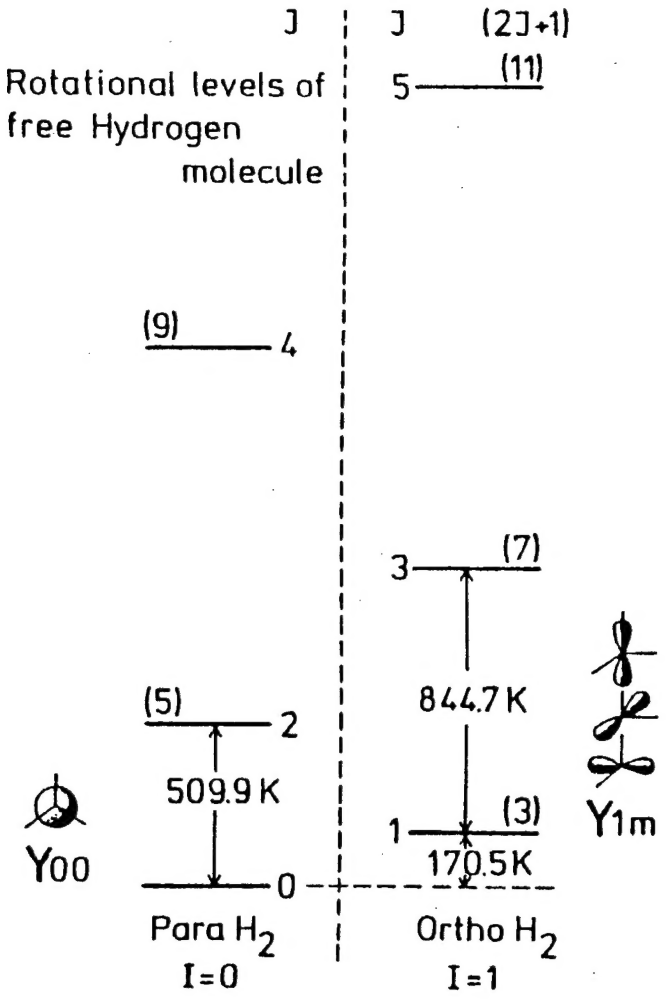
liquid H_2 : = 0.070 g/cm^3
solid H_2 : = 0.087 g/cm^3 (+25%)
50/50 liquid He/solid H_2 : = 0.105 g/cm^3 (+50%)

New ~~CCD~~
SLIDE

Experimental Diagram

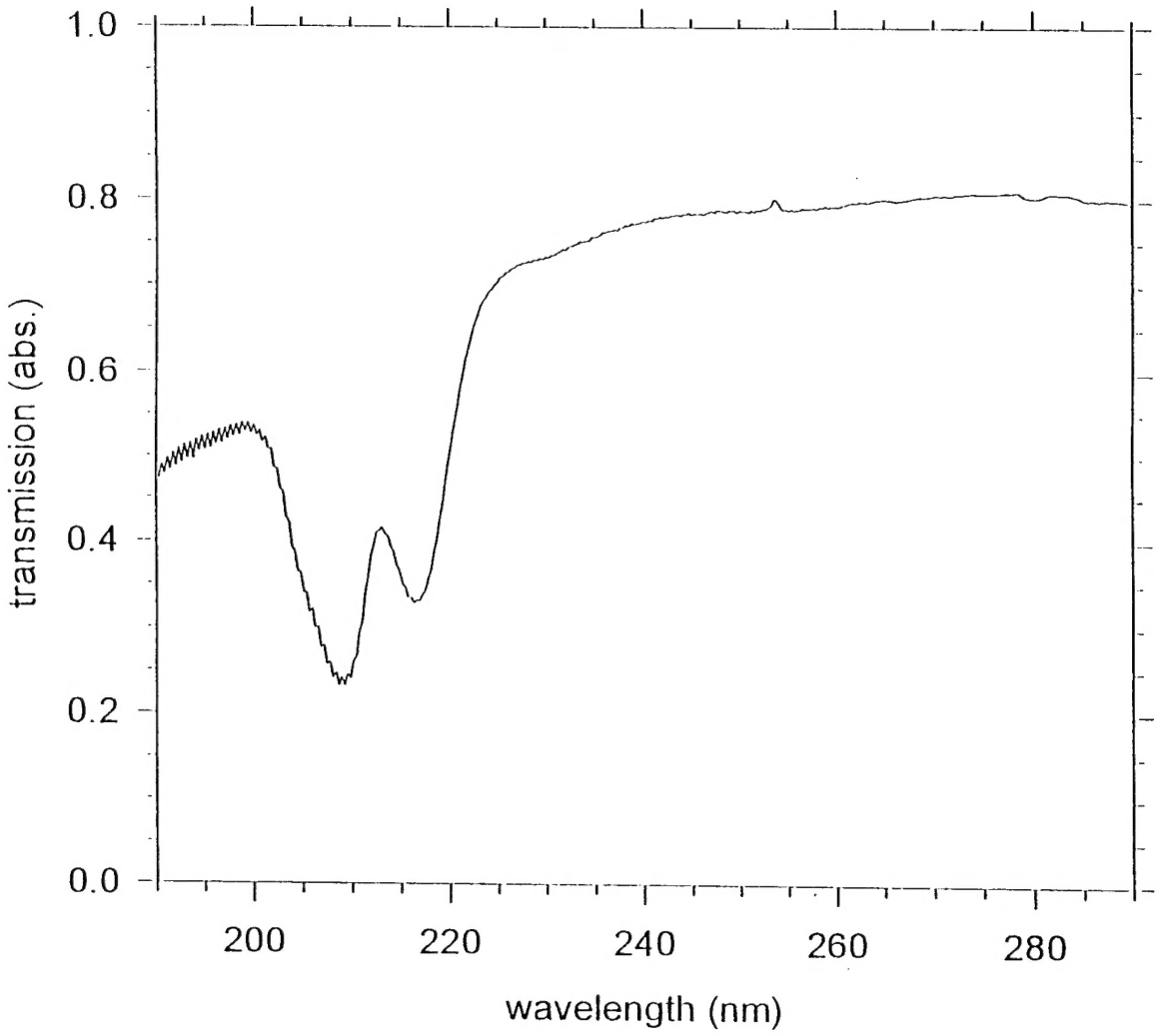


Ortho- and Para-Hydrogen



I.F. Silvera
Rev. Mod. Phys.,
52, 393 (1980).

B Ablation in p-H_2 Matrix Transmission Spectrum at 2 K



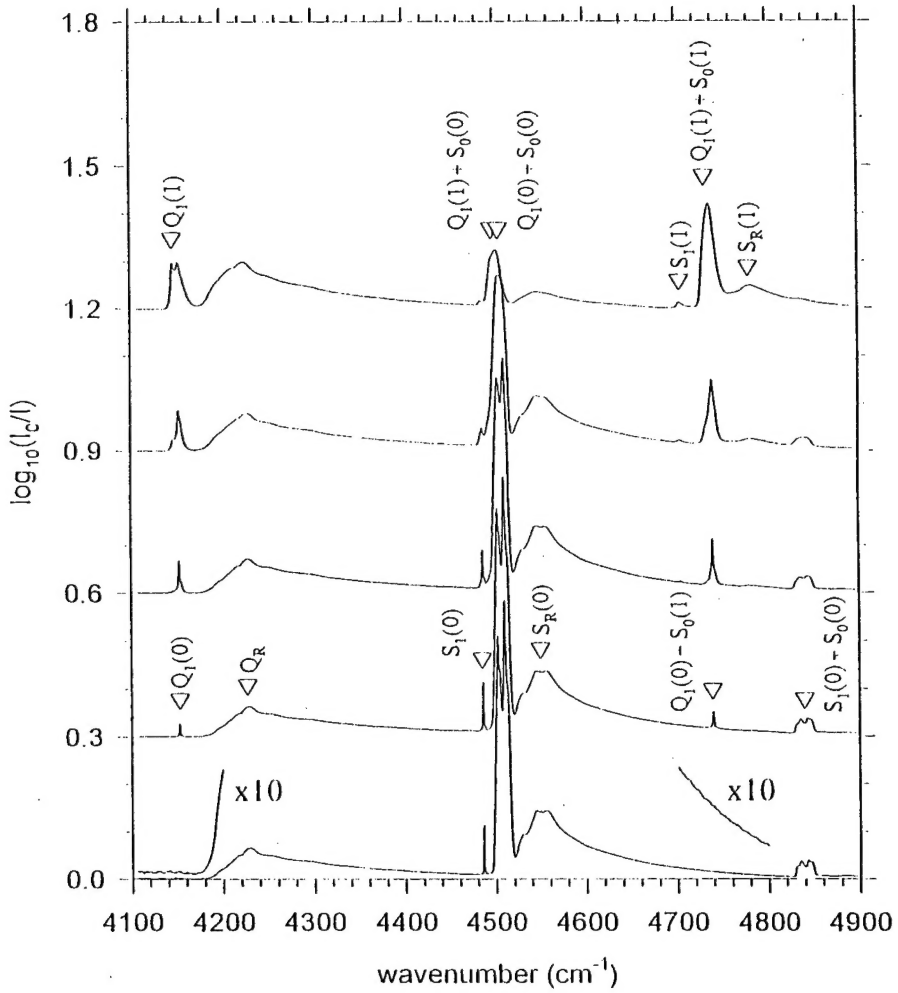
NOTE:
Transmission = 0.8
at 240 nm!

NEW

Demonstration of Control of o-H_2 Fraction

At 0% o-H2:
Observation of $S_1(0)$ and non-observation of $Q_1(0)$ implies h.c.p. solid

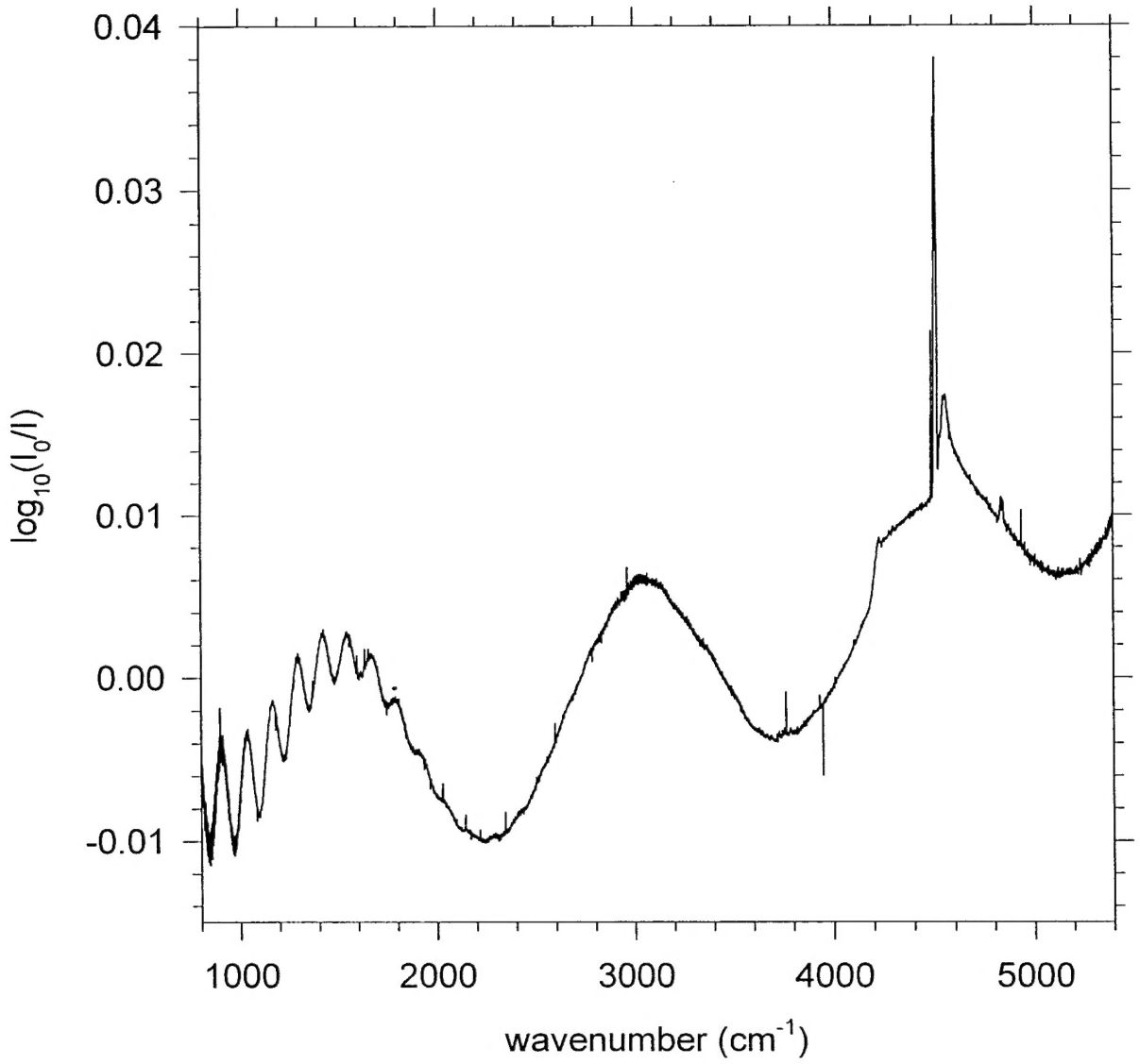
Reference:
J. van Kranendonk & H.P. Gush, Phys. Lett., **1**, 22 (1962).



Convertor Temp	% o-H_2
135 K	70
52 K	25
37 K	8
28 K	2
15 K	< 0.01

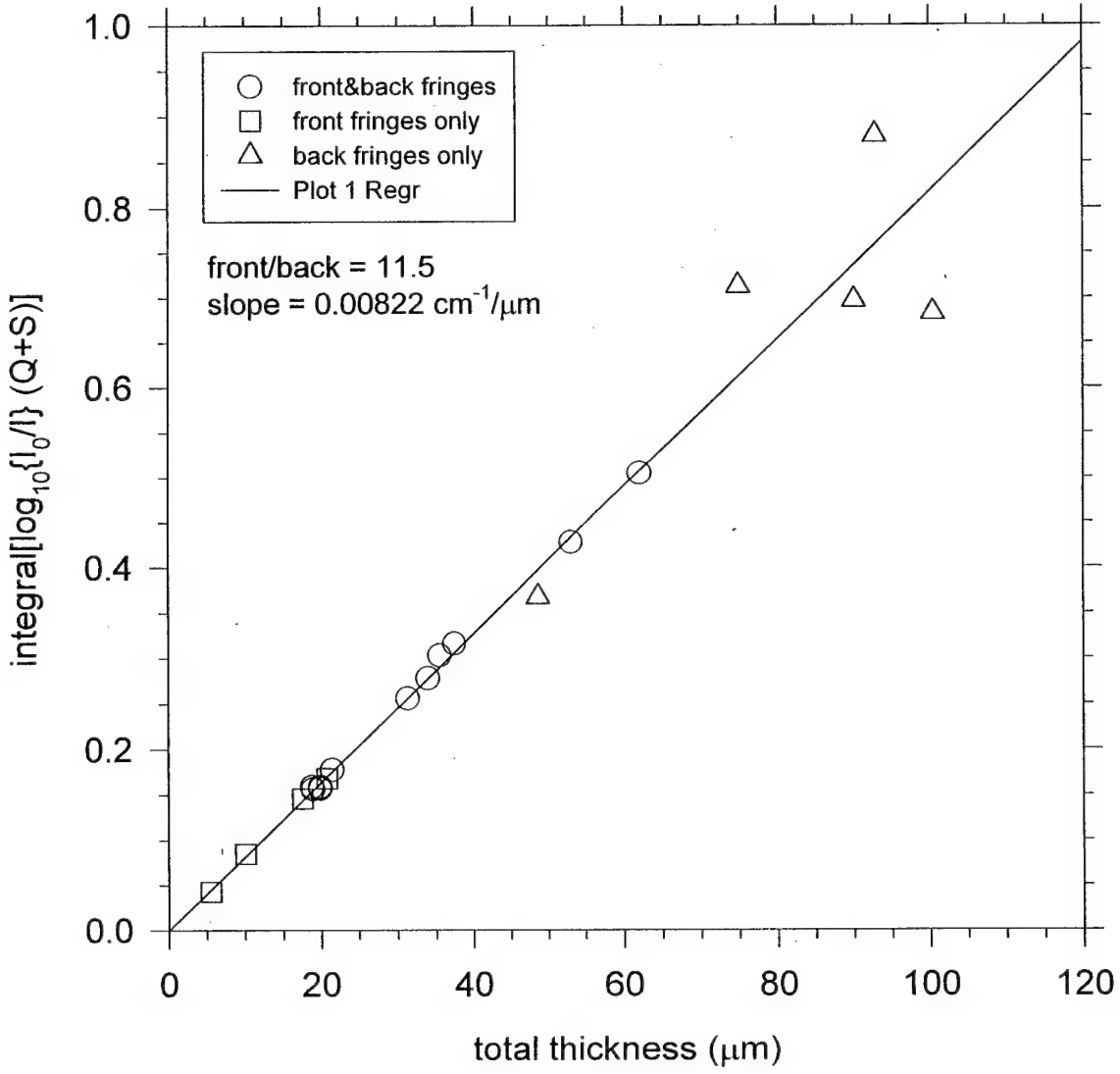
NEW

IR Absorption Spectrum of a 37.4 μm Thick Vapor Deposited pH_2 Solid (34.4 μm front + 3.0 μm back)



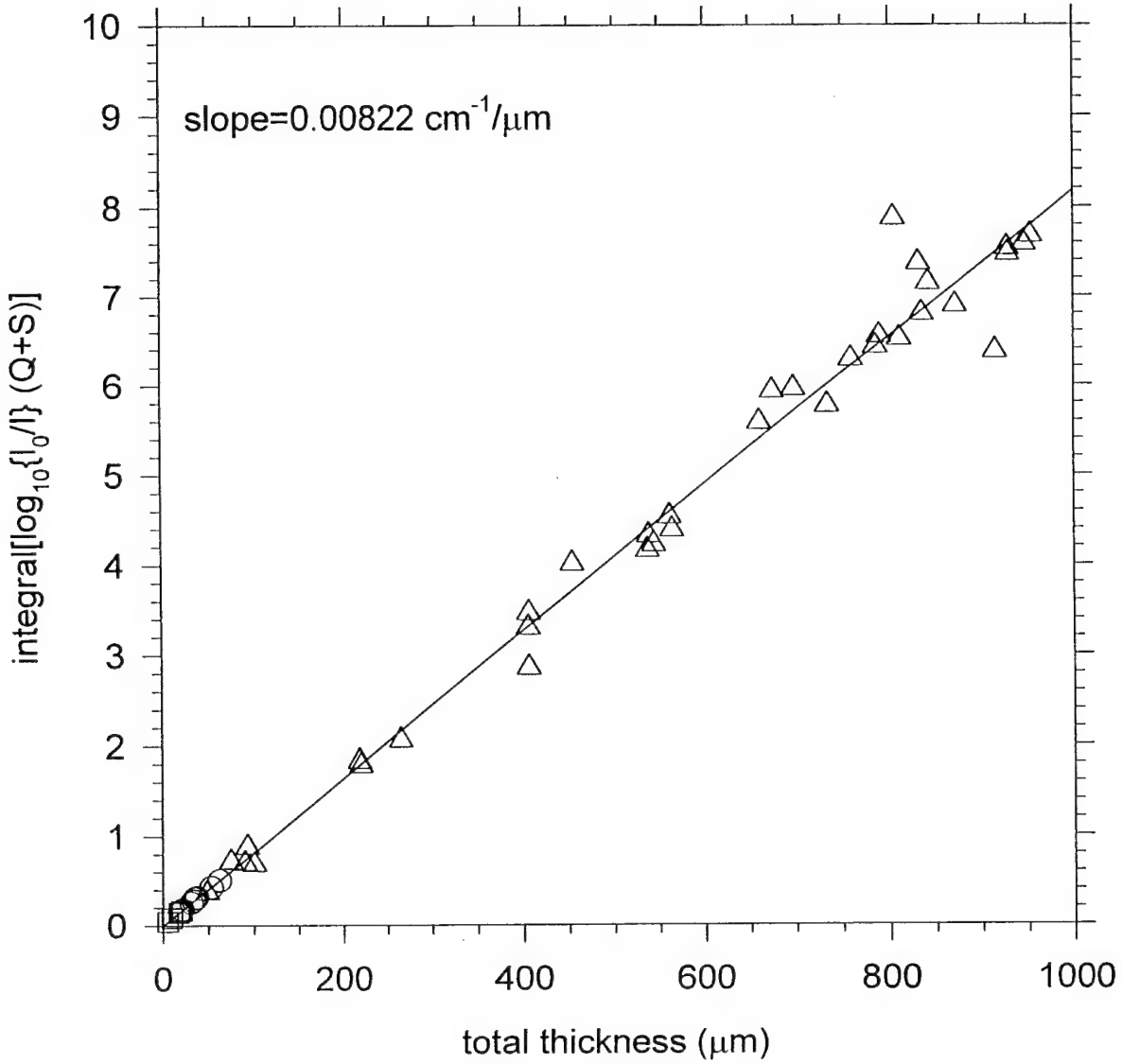
NEW

Correlation of the Total Thickness Determined by Interferometry versus the Integrated Absorption Intensity of the $Q_1(0)+S_0(0)$ Transition of Solid pH_2

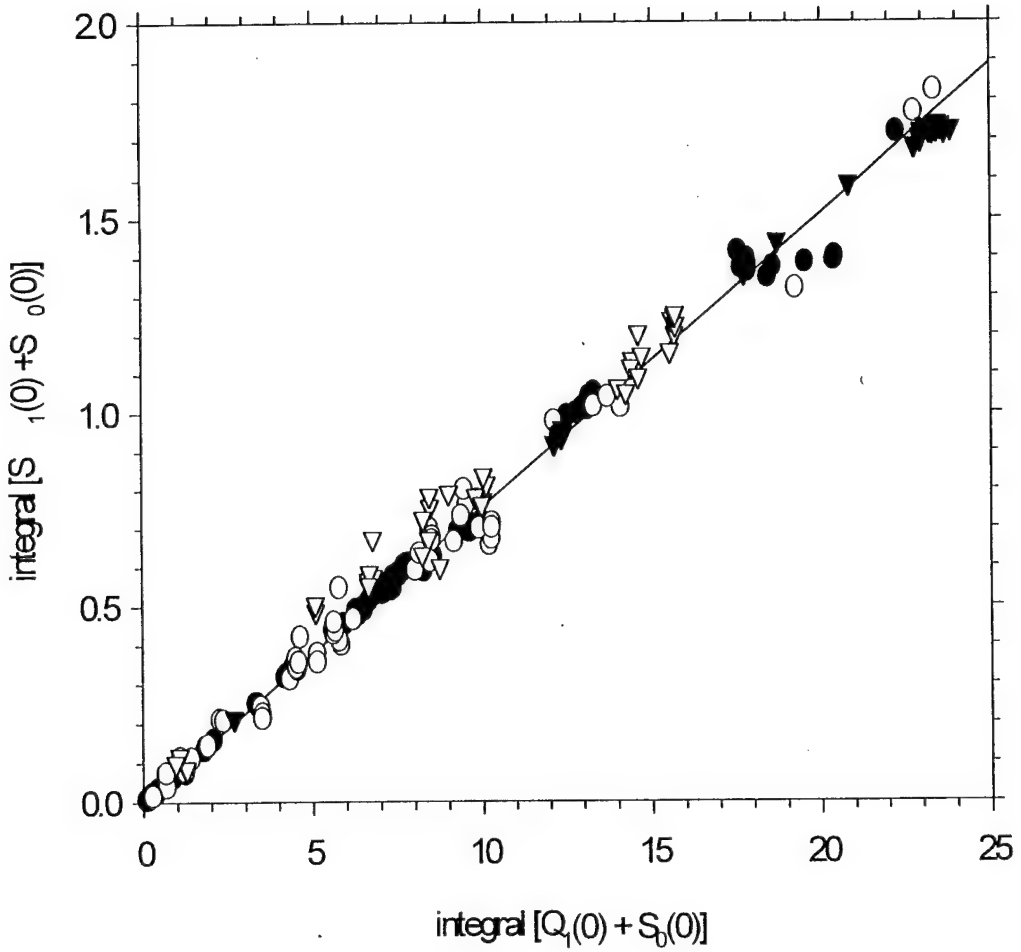


NEW

Extrapolation of the Total Thickness versus the Integrated Absorption Intensity of the $Q_1(0)+S_0(0)$ Transition of Solid pH_2



Correlation between the Integrated Intensities of the $Q_1(0)+S_0(0)$ and $S_1(0)+S_0(0)$ Transitions of Vapor Deposited pH_2 Solids



NOTES

$\alpha_{Q+S} = 188\ cm^{-2}$

$\alpha_{S+S} = 0.0757\ \alpha_{Q+S} = 14.2\ cm^{-2}$

For determining thickness:

Band	Range
$Q_1(0)+S_0(0)$	0-1 mm
$S_1(0)+S_0(0)$	1-10 mm

OLD SLIDE

Beer's Law

$$A(\tilde{\nu}) \equiv 2.303 \quad \log_{10}\left(\frac{I_0}{I}\right) = \alpha c l$$

$$c = \frac{A(\tilde{\nu})}{\alpha\, l} \Rightarrow \frac{2.303 \int_{band} \log_{10}\left(\frac{I_0}{I}\right) d\tilde{\nu}}{l \int_{band} \alpha(\tilde{\nu}) d\tilde{\nu}}$$

Increased path lengths or highly concentrated samples can cause saturation of the absorption.

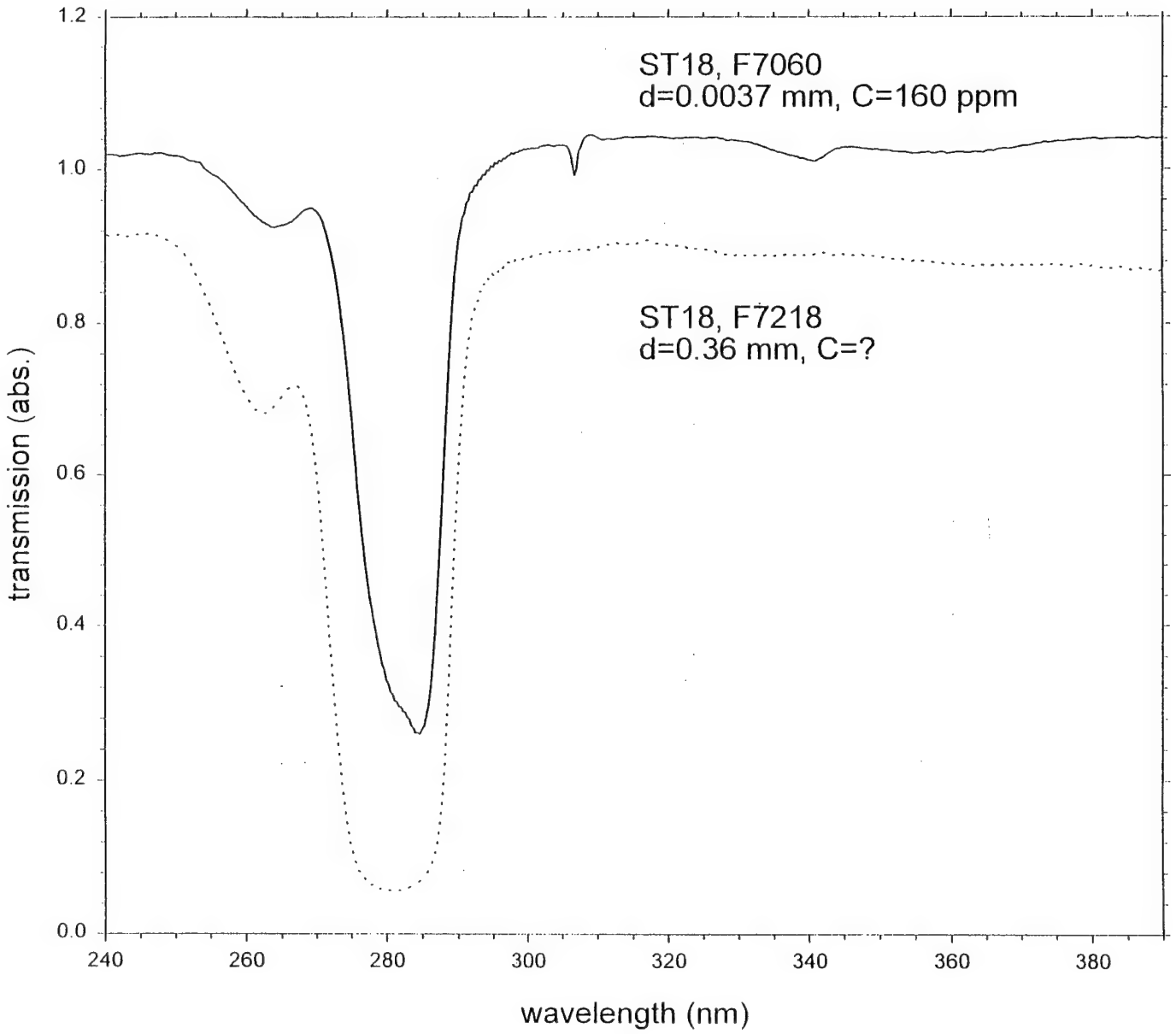
If we want to work with gram scale, heavily-doped pH_2 samples, we require a spectral feature that has a very small intrinsic absorption coefficient (α) to compensate for the higher c and l.

We can use dopant-induced infrared absorptions to determine the concentration.

BUT: Need to determine $\alpha_{ind} \equiv$ the dopant-host intrinsic absorption strength

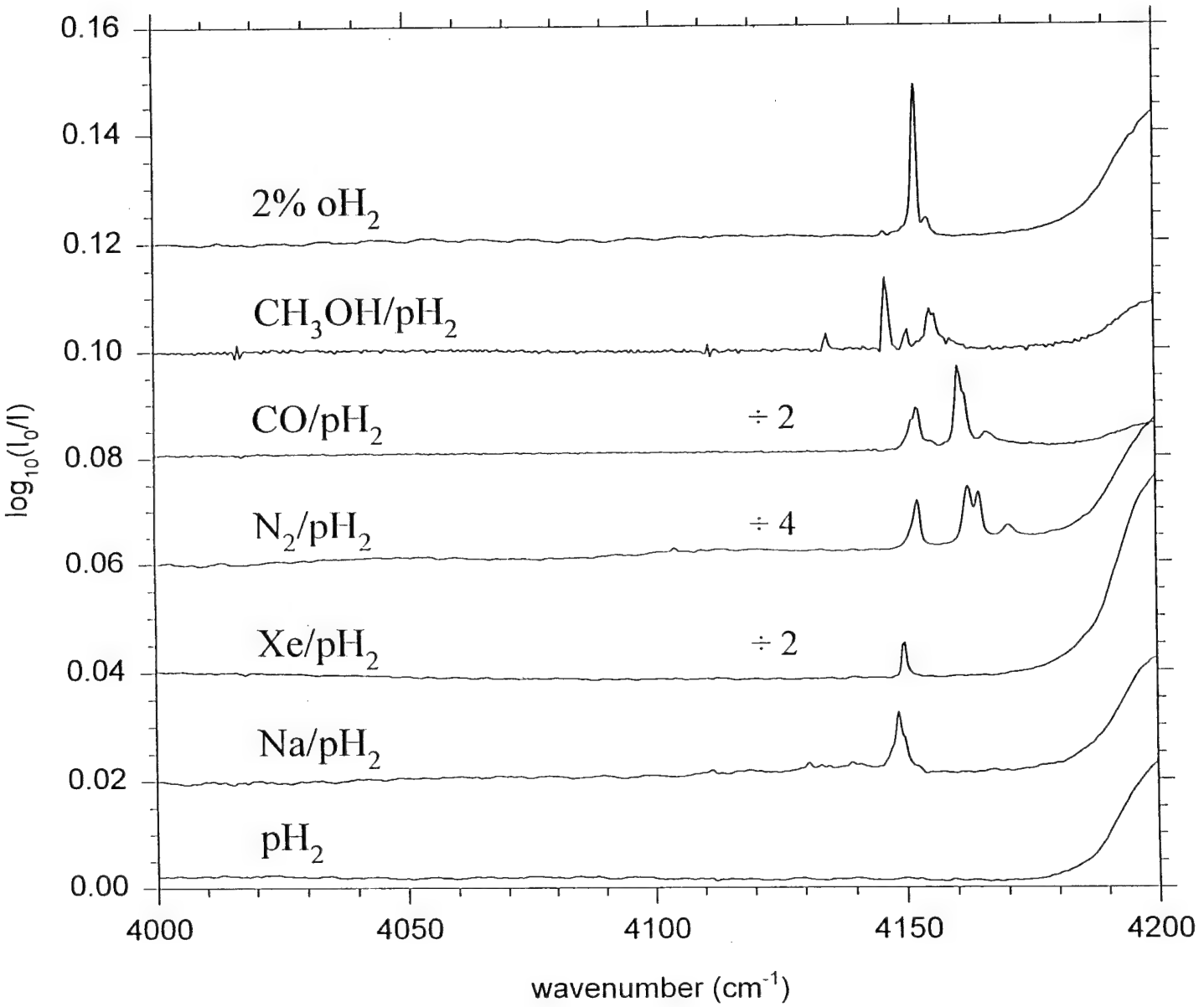
OLD SLIDE

Mg/pH_2 and Mg/oD_2, T=2 K

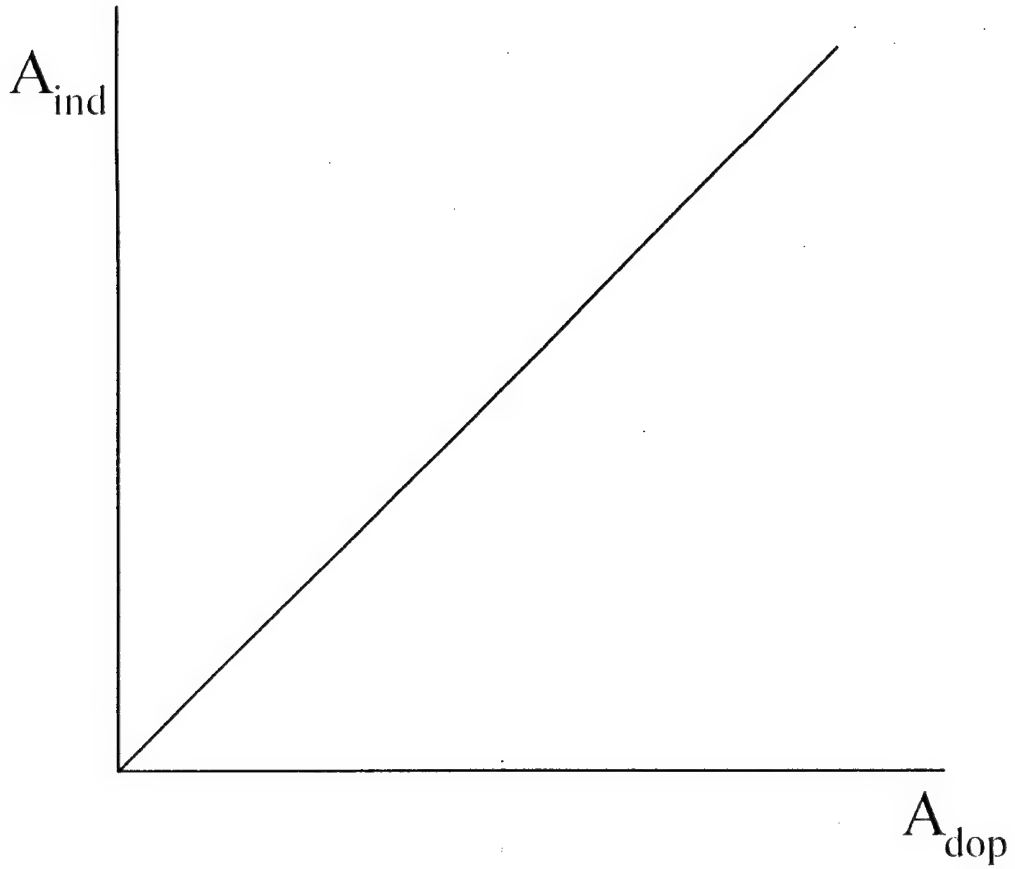


OLD SLIDE

Examples of Dopant Induced H_2 Absorptions



Determining α_{ind} from α



Where:

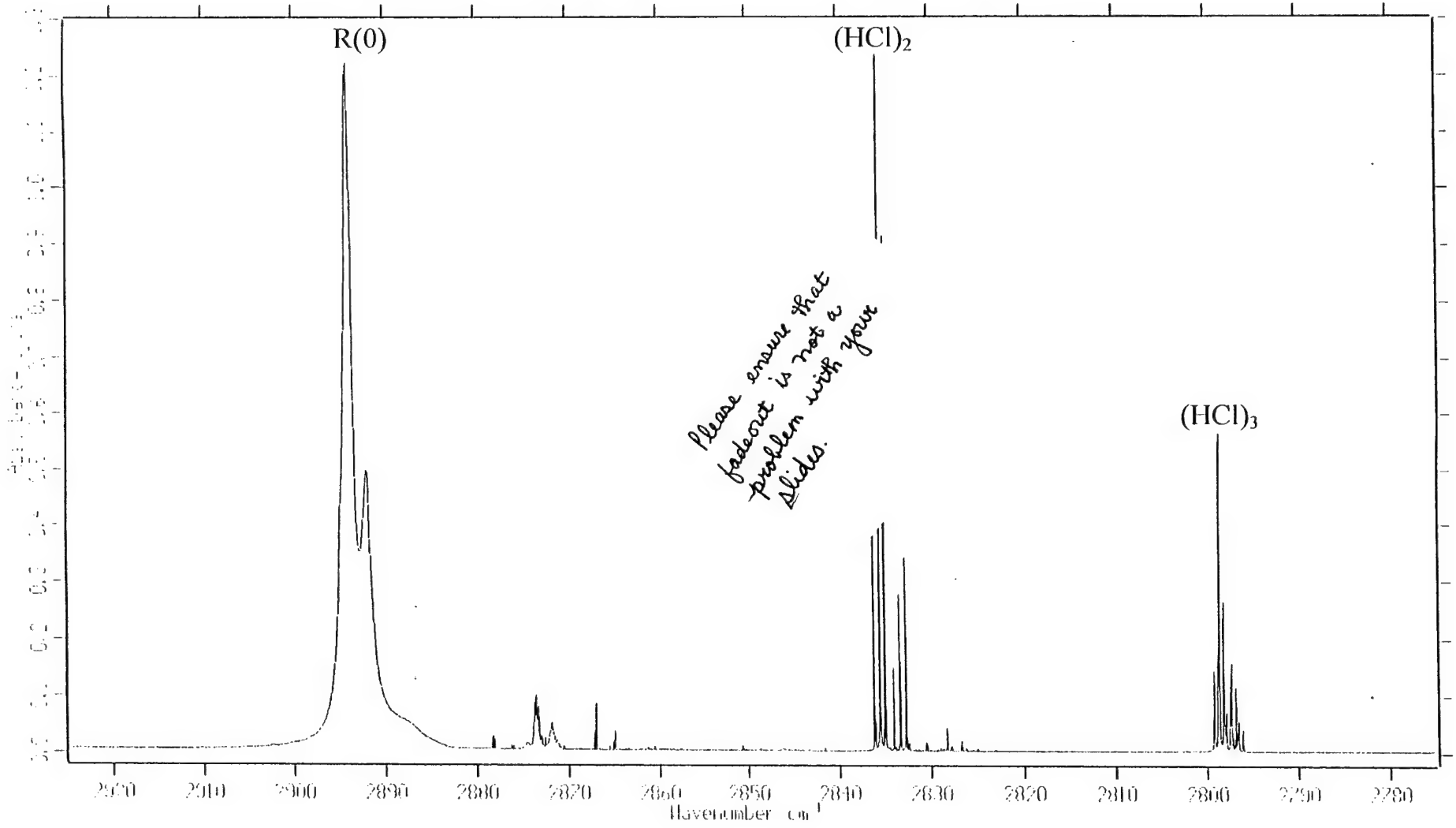
Slope of the line = $\frac{\alpha_{ind}}{\alpha}$

$\alpha \equiv$ property of the dopant in the gas phase

$\alpha_{ind} \equiv$ property of the dopant and pH_2 in solid pH_2

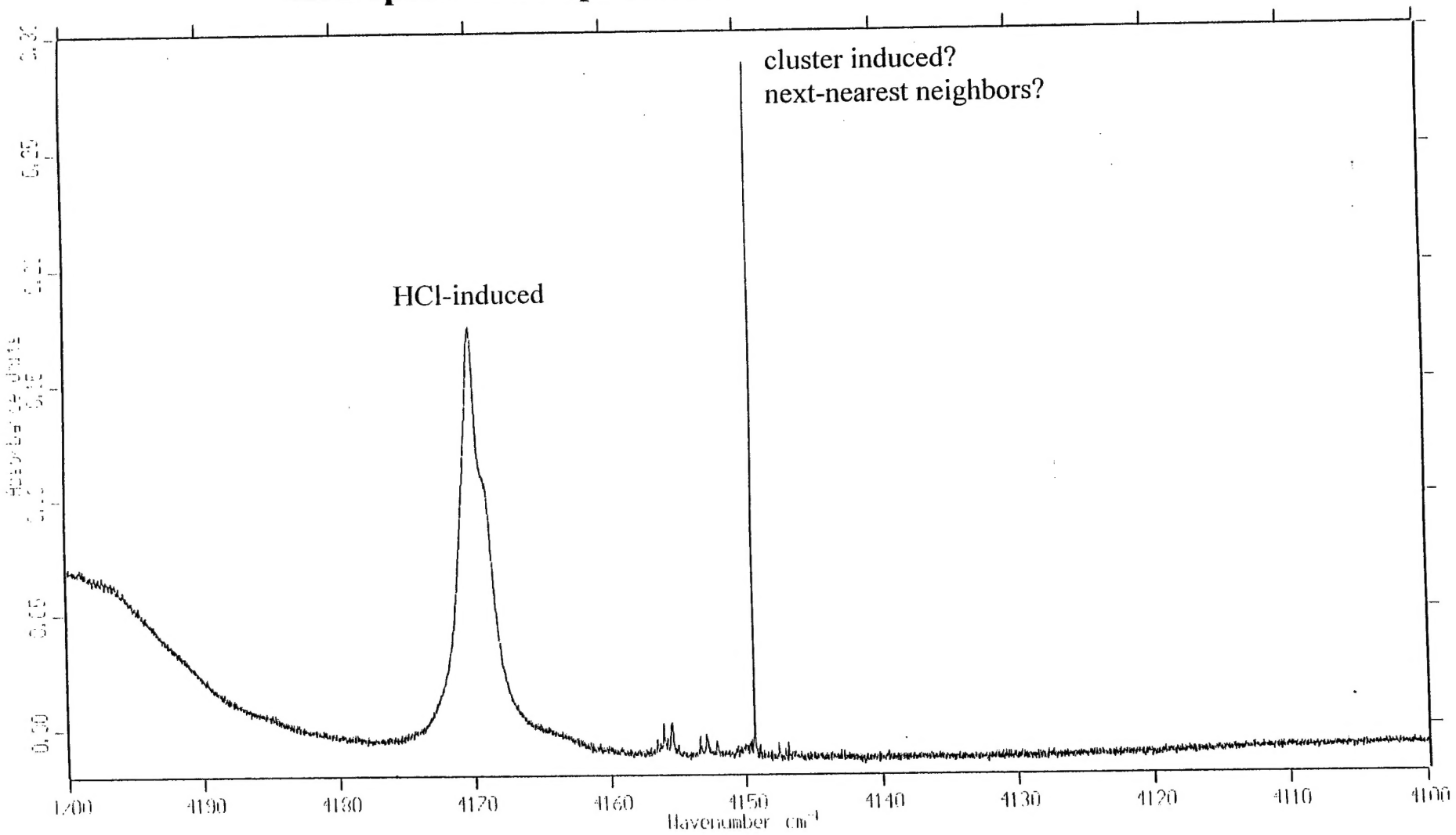
OLD SLIDE

HCl/pH_2 at 2.4 K, 88 ppm, Resolution = 0.0075 cm^{-1}
Annealed Sample, HCl Absorptions Region



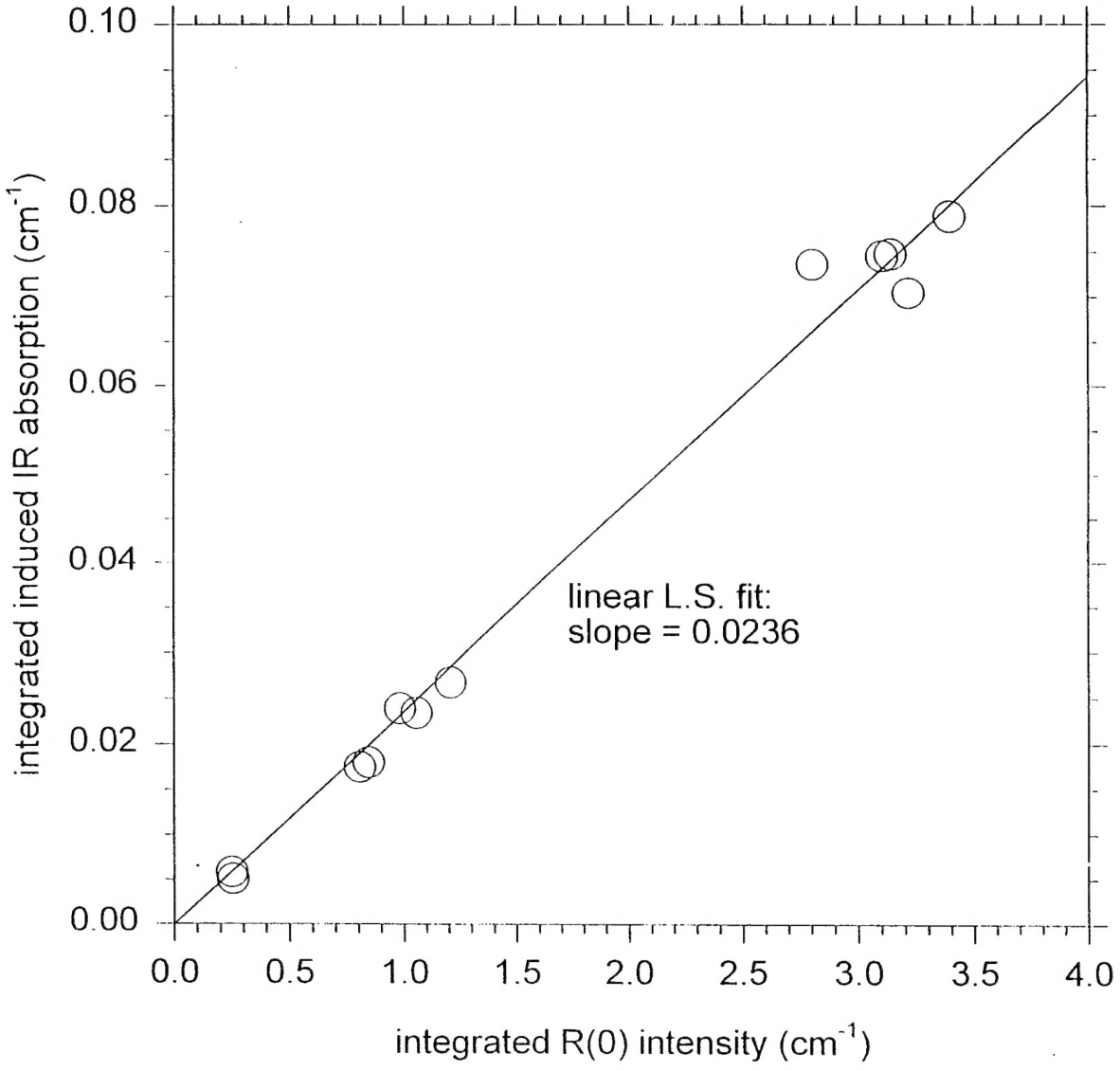
OLI SLIDE

HCl/pH_2 at 2.4 K, 494 ppm, Resolution = 0.0075 cm^{-1}
As Deposited Sample, Induced Absorption Region



OLL SLIDE

Correlation between HCl-Induced pH_2 IR Absorption and HCl R(0) Absorption



HCl-Induced pH_2 Intrinsic IR Absorption Strength

$$\int\alpha_{ind}(HCl/pH_2)d\nu = 0.0236 \int\alpha(HCl)\, d\nu$$

literature: $\int\alpha(HCl)\, d\nu = 19.8$ km/mol*

$$\therefore \quad \int\alpha_{ind}(HCl/pH_2)\, d\nu = \underline{\mathbf{0.47\ km/mol}}$$

*K. N. Rao, ed., *Molecular Spectroscopy: Modern Research Vol. III* (Academic Press, Inc., New York, 1985).

Question: What is the maximum, measurable concentration of HCl/pH_2?

Assume: a) 1 mm thick sample

b) $\int A_{max}\, d\nu = 2\ cm^{-1}$

Answer:

$$c_{max} = \frac{2.303\ (2\ cm^{-1})}{(0.1\ cm)(4.7x10^4\ \frac{cm}{mol})}$$

$$= 9.9 \times 10^{-4}\ mol/cm^3$$

$$\Rightarrow 2.3\%\ HCl/pH_2$$

OLD SLIDE

SUMMARY

For millimeters thick, heavily-doped samples, direct absorption spectroscopy fails because of limitations on dynamic range and achievable signal-to-noise levels.

Dopant-induced pH_2 transitions are a possible solution to this problem.

1) appear to obey Beer's Law
2) are very weak IR transitions (i.e., increased dynamic range for heavily doped samples)

For HCl in pH_2, the intrinsic absorption strength of the induced transition is approximately 2.4% of the intrinsic absorption strength of HCl in the gas phase.

Can calculate the maximum measurable concentration for a HCl-doped pH_2 solid: 2.3% for a 1 mm thick sample, achieving objective of measuring ~1% concentration in millimeters thick samples.

FUTURE DIRECTIONS

We are in the process of completing a survey of various dopants in solid pH_2 to determine the generality of using the induced absorptions for concentration measurements.